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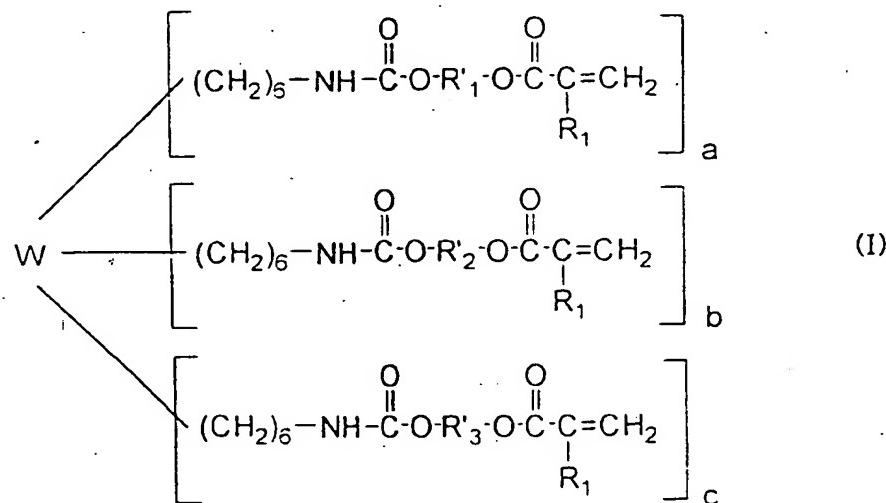
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(54) Photo-curable prepolymer comprising quaternary ammonium salt and process for
preparing thereof

(57) The present invention relates to a photo-curable prepolymer having the following formula (I):

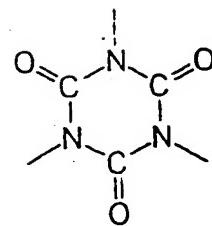
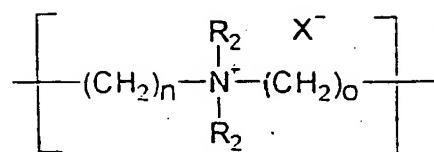


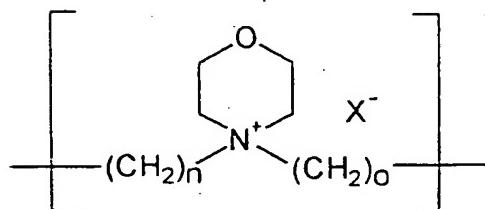
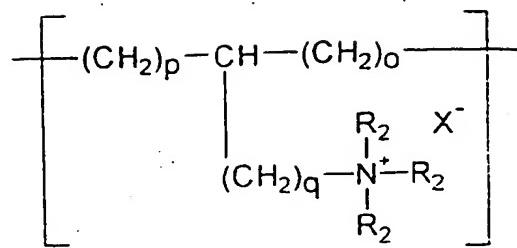
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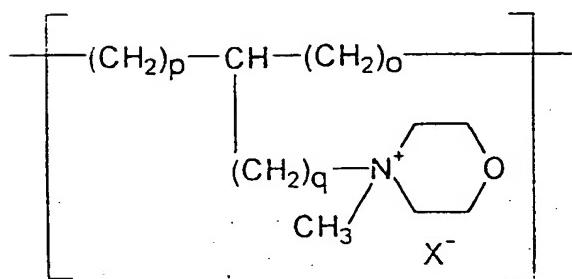
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represents

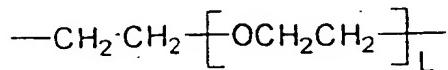
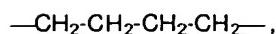
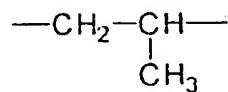
 R_1
 R_1' represents hydrogen or methyl;
represents



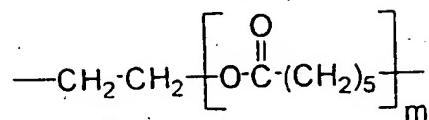
or



wherein X represents chlorine or bromine atom, R₂ represents methyl or ethyl, n, o and q independently of one another denote an integer of 1 to 6 and p denotes an integer of 0 to 6; R₂' and R₃' are identical to or different from each other and represent



wherein L denotes an integer of 0 to 5, or



wherein m denotes an integer of 1 to 6;

a, b and c independently of one another represent a real number of 3 or less, provided that they satisfy the conditions of $0 < a \leq 3$, $0 \leq b$ and/or $c < 3$ and $a + b + c = 3$.

which shows permanent antistatic property by introducing therein an acrylate moiety having quaternary ammonium group and hydroxy group simultaneously, and to a process for preparing thereof.

Description**BACKGROUND OF INVENTION****5 1. Field of Invention**

The present invention relates to a photo-curable prepolymer comprising quaternary ammonium salt. More specifically, the present invention relates to a photo-curable prepolymer which shows permanent antistatic property by introducing therein an acrylate moiety having quaternary ammonium group and hydroxy group simultaneously.

10 The present invention also relates to a process for preparing the photo-curable prepolymer as mentioned above.

2. Background Art

Generally, minute electronic parts used for electric or electronic equipments, household electric appliances, etc., 15 are contained in a plastic case. However, such a plastic case has a tendency to be stained easily by adsorbing dusts which are dispersed through atmosphere since it has static electricity due to the high insulation resistance. Moreover, dusts or static electricity may cause an erroneous operation of the electronic parts. Therefore, it has been recognized that it is essential to finish the electronic parts housing so that any static electricity may not occur.

15 The early stage anti-static agent, however, are conventionally composed of low molecular weight surfactants. And 20 such an anti-static agent forms a surface layer during coating of a plastic product, but it does not show a durable effect because the anti-static layer can easily be washed out. Accordingly, various processes for applying a surface of a plastic finishing product anti-static curable coating materials to have durable antistatic effect have been developed.

25 For example, European Patent Publication No. 0 541 289 A1 discloses a method for the preparation of polyurethane prepolymer having quaternary ammonium salt. This Patent also teaches that a difunctional urethane acrylate latex or water-dispersions thereof can be produced by using the prepolymer and that thus produced latex can be used as a photo-curable coating material. But, the above Patent has focused their attention merely on a chemical structure of the cationic polyurethane to increase the water-dispersibility of the prepolymer, and there is no mention on their anti-static effect.

30 In addition, an UV curable antistatic hard-coatings manufactured from polymeric antistatic agent and conventional UV curable coating materials are described in Radtech Asia '93 (P492-498, Nov. 10-13, 1993). However, this cannot be applied practically because a mechanical strength of the UV curable antistatic hard-coatings becomes weaker than that of the early-stage coating materials due to the low cross-linking density. Thus, it has been required to develop a new prepolymer which shows a permanent antistatic property and simultaneously is useful for manufacturing of non-solvent type photo-curable coating material.

35 Accordingly, the present inventors have focussed their attention on this point and have extensively studied for a long time. As a result, they found an astonishing fact that a photo curable coating material prepared from a specific prepolymer, i.e., aliphatic trifunctional urethane acrylate prepolymer made from hydroxy alkyl acrylate having quaternary ammonium salt, shows a permanent antistatic property and an excellent staining resistance, and thus completed the present invention.

40 Therefore, it is an object of the present invention to provide an aliphatic trifunctional urethane acrylate prepolymer useful for preparing a photo-curable resin composition.

It is another object of the present invention to provide a process for preparing the photo-curable prepolymer as mentioned above.

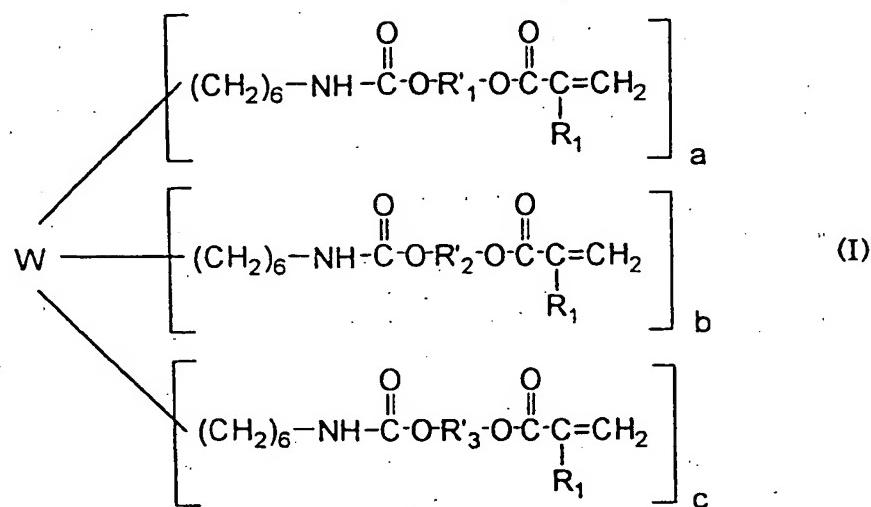
45 The foregoing has outlined some of the more pertinent objects of the present invention. These objects should be construed to be merely illustrative of some of the more pertinent features and applications of the invention. Many other beneficial results can be obtained by applying the disclosed invention in a different manner or modifying the invention within the scope of the disclosure. Accordingly, other objects and a more thorough understanding of the invention may be had by referring to the disclosure of invention, in addition to the scope of the invention defined by the claims.

DISCLOSURE OF INVENTION

In one aspect, the present invention relates to a photo-curable aliphatic trifunctional urethane acrylate prepolymer having the following formula (I) :

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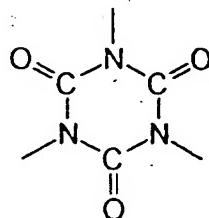
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in which

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W represents

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R₁ represents hydrogen or methyl;

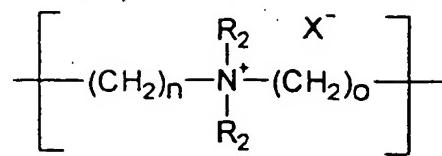
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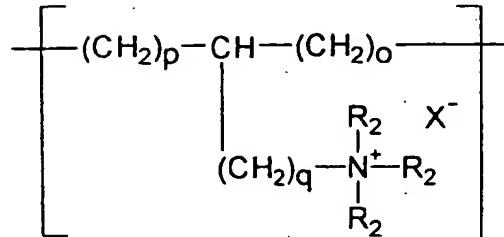
R₁ represents

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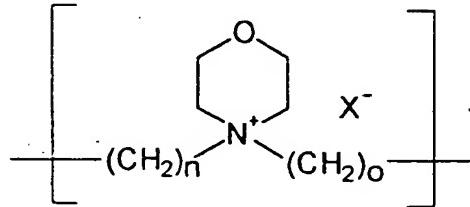
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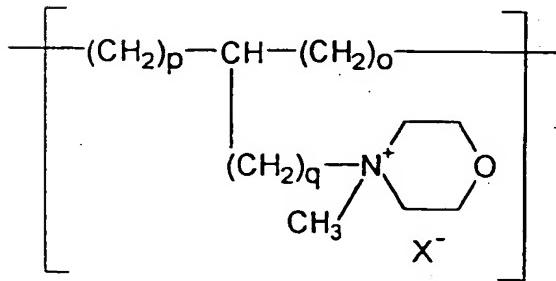
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or

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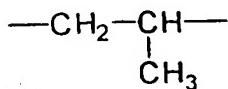
wherein X represents chlorine or bromine atom, R₂ represents methyl or ethyl, n, o and q independently of one another denote an integer of 1 to 6 and p denotes an integer of 0 to 6;

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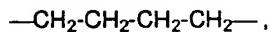
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R_{2'} and R_{3'} are identical to or different from each other and represent

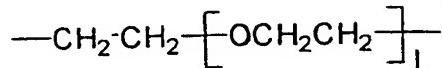
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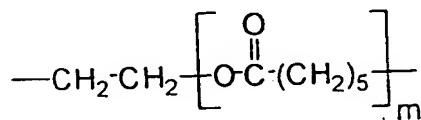


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wherein L denotes an integer of 0 to 5, or



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wherein m denotes an integer of 1 to 6;

a, b and c independently of one another represent a real number of 3 or less, provided that they satisfy the conditions of $0 < a \leq 3$, $0 \leq b$ and/or $c < 3$ and $a + b + c = 3$.

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In the second aspect, the present invention relates to a process for preparation of the photo-curable prepolymer of the above formula (I) by reacting an aliphatic multifunctional isocyanate having the following formula (II) with a quaternary ammonium salt having the following formula (III), optionally with the compound of the following formula (IV) and/or that of the following formula (V).

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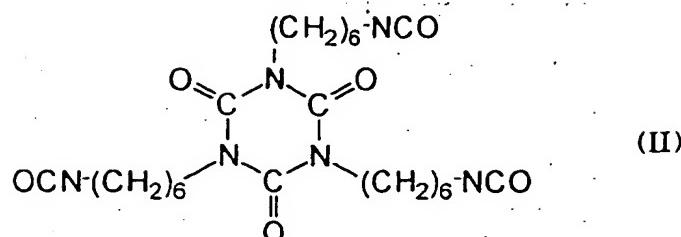
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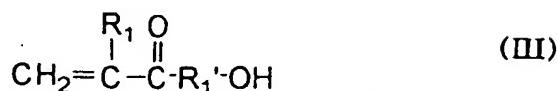
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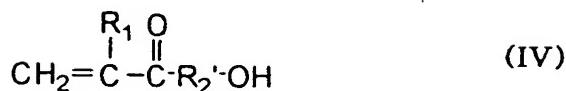


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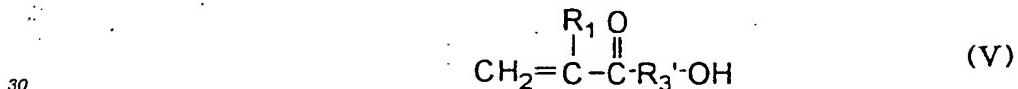
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In the above formulas,

R_1 , R_1' , R_2' and R_3' are defined as previously described.

The aliphatic multifunctional isocyanate of formula (II) which can be used in this reaction includes isocyanurate type trimers of isophorone diisocyanate or hexamethylene diisocyanate. Among them, isocyanurate type trimer of hexamethylene diisocyanate is more preferable, and as its commercially available articles, Luxate HT2000 (Olin Corp.) and Coronate HX (Nippon Polyurethane Ind. Co., Ltd.) can be mentioned.

One of the most important characteristics of the photo-curable prepolymer according to the present invention is that the quaternary ammonium salt of formula (III) is introduced therein. The quaternary ammonium salt of formula (III) has quaternary ammonium group and hydroxy group. Among these two groups, the quaternary ammonium group contributes to improve the antistatic property and staining resistance of the produced final coating material, and the hydroxy group is reacted with the isocyanate functional group of formula (II) to produce the desired prepolymer.

In order to improve the physicochemical properties such as flexibility or adhesion strength, etc. of the photo-cured resin composition which can be prepared from the prepolymer according to the present invention, it is preferable that the compounds of formula (IV) and/or (V) are mixed with the quaternary ammonium salt of formula (III) and then the mixture is reacted with the aliphatic multifunctional isocyanate of formula (II) to prepare the aliphatic trifunctional urethane acrylate prepolymer of formula (I).

The compounds of formulas (IV) and (V) are hydroxyalkyl methacrylate (or hydroxyalkyl acrylate) compounds which have methacryl (or acryl) and hydroxy functional groups in their structure and at the same time do not include any quaternary ammonium salts. These compounds (IV) and (V) are optionally used to control the physicochemical properties (for example, flexibility) of the prepolymer (I) according to the present invention. The compounds of formulas (IV) and (V) used herein include hydroxyethyl(meta)acrylate, hydroxypropyl(meta)acrylate or hydroxybutyl acrylate, however, they are not restricted only to these.

As their commercially available articles, hydroxyethyl acrylate, hydroxypropyl acrylate, Sipomer HEM (Rhone-Poulenc), Placcel (Daicel Chemical Ind., Ltd.) and Tone Monomer (Union Carbide Co.) can be mentioned.

It is preferable to use the total hydroxy groups which exist in the compounds of formula (III), (IV) and (V) in a ratio of 1 : 1 equivalents with respect to the isocyanate groups in the compound of formula (II). It is also preferable to use the hydroxy group in the compound of formula (III) in a ratio of 1/10 to 2/3 equivalents with respect to the isocyanate groups

in the compound of formula (II). There is no restriction on the ratio between the amount of the compounds (III), (IV) and (V) used, that is, on the ratio between a, b and c in the formula (I), but it is preferable that a is 0.3 to 2.0 when the sum of a, b and c is 3. In case a exceeds 2.0, there can occur some deterioration in the flexibility and gloss of the product.

By introducing the prepolymer prepared according to the present method into the photo-curable resin composition, permanent antistatic property and improved staining resistance of the product can be obtained.

The present invention will be more specifically explained in the following examples. However, it should be understood that the following preparations and examples are intended to illustrate the present invention and not to limit the scope of the present invention in any manner.

10 Example 1

Synthesis of metacryloxyethylidimethyl(hydroxyethyl) ammonium bromide

31.4g (0.2 mole) of (dimethylamino)ethyl metacrylate was introduced into a 250 ml three-neck flask equipped with ice-bath, thermometer, refluxing condenser, dropping funnel and magnetic stirring bar. The compound was stirred and then the temperature was lowered to -10°C. 25g (0.2 mole) of bromoethanol was added dropwise thereto over 30 minutes while maintaining the temperature of the contents at 0°C or less. After completion of dropping, the reaction mixture was stirred for 24 hours at room temperature. 100ml of ethyl acetate was added to the mixture and the whole was stirred, filtered and dried to obtain 54g (Yield: 96%) of the title compound as a white powder.

20 ^1H NMR (DMSO-d₆, 300MHz): δ 6.18(1H), 5.85(t,J=1.5Hz,1H), 5.43(t,J=5.1,1H), 4.63(br.s,2H), 3.95(br.m, 2H), 3.88(br.m,2H), 3.62(br.t,J=5.4,4.5Hz, 2H), 3.26(s,6H), 2.0(s,3H)

25 Example 2

25 74.50g (0.264 mole) of metacryloxyethylidimethyl(hydroxyethyl) ammonium bromide prepared in Example 1, 204.3712g (1.76 mole) of hydroxyethyl acrylate and 211.904g (0.616 mole) of caprolactone modified hydroxyethyl acrylate (Tone M-100 ; UCC Co.) were mixed together to produce a monomer mixture. On the other hand, 473.2392g (0.800 mole) of isocyanurate type trimer of 1,6-hexamethylene diisocyanate (Coronate-HX ; Nippon Polyurethane Ind. Co., Ltd.), 0.048g of dibutyl tin dilaurate as a catalyst and 0.241g of octadecyl-3-(3,5-di-tertbutyl-4-hydroxyphenyl)propionate (Irganox 1076 : Ciba-Geigy Co.) as a radical scavenger were introduced into a reactor equipped with thermometer, and the temperature of the contents was controlled to 50°C while stirring at a rate of 200 rpm. After controlling was completed, the previously prepared monomer mixture was added dropwise thereto over 2 hours with blowing the air up, during which the reaction temperature was maintained to less than 60°C. After addition, the temperature of the contents was elevated to 80°C and 0.096g of dibutyl tin dilaurate was added thereto and then the mixture was reacted for more than 2 hours. 0.048g (about 50ppm) of TNPP (tris(nonylphenyl)phosphite) was added as a stabilizer for completing the reaction, and consequently about 964g of the prepolymer of which weight percent of NCO group is 0.0 (ASTM D 2572-80) and the Number Average Molecular Weight is 1970 (GPC, measured by CHCl₃) was obtained.

40 ^1H NMR (CDCl₃, 300 MHz): δ 4.3(-COOCH₂CH₂OCO-), 3.5 (CH₃*NCH₃Br⁻), 3.2-3.0(-NHCOO-), 2.2-2.3 (-CH₂COO-)

Example 3

45 225.8g (0.8 mole) of metacryloxyethylidimethyl(hydroxyethyl) ammonium bromide prepared in Example 1 and 255.5g (2.2 mole) of hydroxyethyl acrylate were mixed together to produce a monomer mixture. On the other hand, 591.55g (1.0 mole) of isocyanurate type trimer of 1,6-hexamethylene diisocyanate (Coronate-HX ; Nippon Polyurethane Ind. Co., Ltd.), 0.05g of dibutyl tin dilaurate as a catalyst and 0.27g of octadecyl-3-(3,5-di-tertbutyl-4-hydroxyphenyl)propionate (Irganox 1076 : Ciba-Geigy Co.) as a radical scavenger were introduced into a reactor equipped with thermometer, and the temperature of the contents was controlled to 50°C while stirring at a rate of 200 rpm. After controlling was completed, the previously prepared monomer mixture was added dropwise thereto over 2 hours with blowing the air up, during which the reaction temperature was maintained to less than 60°C. After addition, the temperature of the contents was elevated to 80°C and 0.1g of dibutyl tin dilaurate was added thereto and then the mixture was reacted for more than 2 hours. 0.05g (about 50ppm) of TNPP (tris(nonylphenyl)phosphite) was added as a stabilizer for completing the reaction, and consequently about 1073g of the prepolymer of which weight percent of NCO group is 0.0 (ASTM D 2572-80) and the Number Average Molecular Weight is 1520 (GPC, measured by CHCl₃) was obtained.

55 ^1H NMR (CDCl₃, 300 MHz): δ 4.3(-COOCH₂CH₂OCO-), 3.5 (CH₃*NCH₃Br⁻), 3.2-3.0(-NHCOO-)

Comparative Example 1

306g (2.6 mole) of hydroxyethyl acrylate and 227g (0.66 mole) of caprolactone modified hydroxyethyl acrylate were mixed together to produce a monomer mixture. On the other hand, 591.55g (1.0 mole) of isocyanurate type trimer of 1,6-hexamethylene diisocyanate (Coronate-HX ; Nippon Polyurethane Ind. Co., Ltd.), 0.05g of dibutyl tin dilaurate as a catalyst and 0.27g of octadecyl-3-(3,5-di-tertbutyl-4-hydroxyphenyl)propionate (Irganox 1076 : Ciba-Geigy Co.) as a radical scavenger were introduced into a reactor equipped with thermometer, and the temperature of the contents was controlled to 50°C while stirring at the rate of 200 rpm. After controlling was completed, the previously prepared monomer mixture was added dropwise thereto over 2 hours with blowing the air up, during which the reaction temperature was maintained to less than 60°C. After addition, the temperature of the contents was elevated to 80°C and then the mixture was reacted for more than 2 hours. 0.05g (about 50ppm) of TNPP (tris(nonylphenyl)phosphite) was added as a stabilizer for completing the reaction, and consequently about 1124g of the prepolymer of which weight percent of NCO group is 0.0 (ASTM D 2572-80) and the Number Average Molecular Weight is 2220 (GPC, measured by CHCl_3) was obtained.

15 ^1H NMR (CDCl_3 , 300 MHz): δ 4.3(-COOCH₂CH₂OCO-), 3.2-3.0 (-NHC_{OO}-), 2.2-2.3(-CH₂COO-)

Application Example 1

50g of the prepolymer prepared in Example 2, 25g of hydroxyethyl acrylate, 15g of hexanediol diacrylate, 5g of trimethylolpropane triacrylate, 4g of 1-hydroxycyclohexyl phenyl ketone (of which trade mark is Irgacure 184 ; Ciba-Geigy Co.) as a photoinitiator and 1g of polyether modified dimethylsiloxane copolymer (of which trade mark is BYK-307 ; BYK-Chemie GmbH) as a levelling agent were thoroughly mixed together to prepare a photo-curable resin composition. A glass plate was coated with that resin composition in a thickness of 10 μm and cured with 80W/cm medium pressure mercury lamp on the conventional UV equipment. The cured resin film was peeled from the glass plate. The physicochemical properties of thus obtained free-standing cured film are described in the following Table 1.

Application Example 2

50g of the prepolymer prepared in Example 3, 25g of hydroxyethyl acrylate, 15g of hexanediol diacrylate, 5g of trimethylolpropane triacrylate, 4g of 1-hydroxycyclohexyl phenyl ketone (of which trade mark is Irgacure 184 ; Ciba-Geigy Co.) as a photoinitiator and 1g of polyether modified dimethylsiloxane copolymer (of which trade mark is BYK-307 ; BYK-Chemie GmbH) as a levelling agent were thoroughly mixed together to prepare a photo-curable resin composition. A glass plate was coated with that resin composition in a thickness of 10 μm and cured with 80W/cm medium pressure mercury lamp on the conventional UV equipment. The cured resin film was peeled from the glass plate. The physicochemical properties of thus obtained free-standing cured film are described in the following Table 1.

Application Example 3

5g of the prepolymer prepared in Example 2, 45g of the prepolymer prepared in Comparative Example 1, 25g of hydroxyethyl acrylate, 15g of hexanediol diacrylate, 5g of trimethylolpropane triacrylate, 4g of 1-hydroxycyclohexyl phenyl ketone (of which trade mark is Irgacure 184 ; Ciba-Geigy Co.) as a photoinitiator and 1g of polyether modified dimethylsiloxane copolymer (of which trade mark is BYK-307 ; BYK-Chemie GmbH) as a levelling agent were thoroughly mixed together to prepare a photo-curable resin composition. A glass plate was coated with that resin composition in a thickness of 10 μm and cured with 80W/cm medium pressure mercury lamp on the conventional UV equipment. The cured resin film was peeled from the glass plate. The physicochemical properties of thus obtained free-standing cured film are described in the following Table 1.

Application Example 4

50g of the prepolymer prepared in Comparative Example 1, 25g of hydroxyethyl acrylate, 15g of hexanediol diacrylate, 5g of trimethylolpropane triacrylate, 4g of 1-hydroxycyclohexyl phenyl ketone (of which trade mark is Irgacure 184 ; Ciba-Geigy Co.) as a photoinitiator and 1g of polyether modified dimethylsiloxane copolymer (of which trade mark is BYK-307 ; BYK-Chemie GmbH) as a levelling agent were thoroughly mixed together to prepare a photo-curable resin composition. A glass plate was coated with that resin composition in a thickness of 10 μm and cured with 80W/cm medium pressure mercury lamp on the conventional UV equipment. The cured resin film was peeled from the glass plate. The physicochemical properties of thus obtained free-standing cured film are described in the following Table 1.

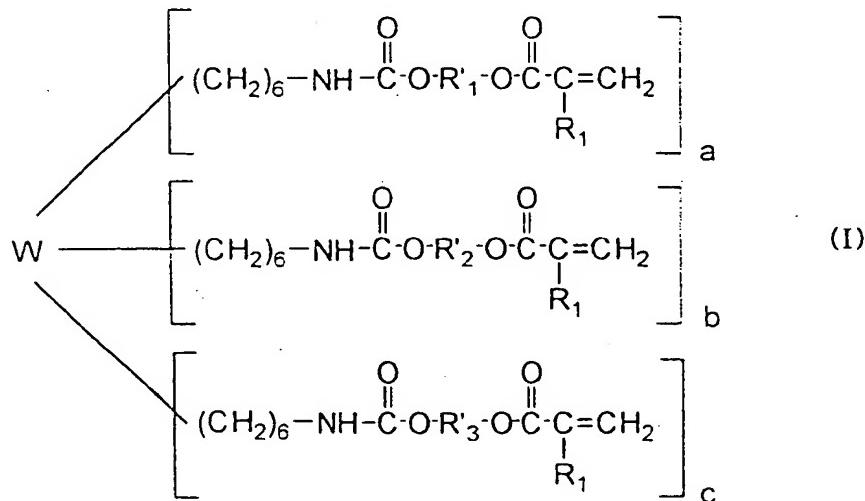
Table 1

		Appn. EX.1	Appn. EX.2	Appn. EX.3	Appn. EX. 4
5	Prepolymer used	EX.2	EX.3	COM.EX.1 + EX.2	COM.EX.1
10	Surface Resistance (Ω)	Initial	10^{12}	10^{11}	10^{13}
	After 2 months		10^{12}	10^{11}	10^{13}
15	Electrostatic Decay Time (mili second, 50% Cut Off)	0.2	0.1	0.5	$>10^5$
20	Flexibility (mm)	3.2	3.2	3.2	3.2
25	Adhesion Strength	100/100	100/100	100/100	100/100
	Staining Resistance	1	1	1	2

* Note :
 Surface Resistance : ASTM D-257
 Electrostatic Decay Time : 5kV DC Charge
 Flexibility : Minimum diameter at which the test sample does not break by Cylindrical Mandrel Test (ASTM D-522)
 Staining Resistance : Scribble on the coated glass plate using an oil magic marker and wipe it out by tissue paper.
 Then, determine the staining level.
 There remains no traces (1);
 there remains some traces (2); and the scribble does not erased (3).
 Adhesion Strength : Cut the 100 crosshatch lines on the coated polyvinylchloride sheet in a width of 1mm and then calculate the number of coating layers which remains on the plate after detaching them from the plate using adhesive tape.

Claims

30 1. A photo-curable prepolymer having the following formula (I) :



in which

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represents

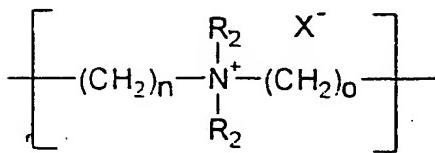
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 R_1
 R_1' represents hydrogen or methyl;
represents

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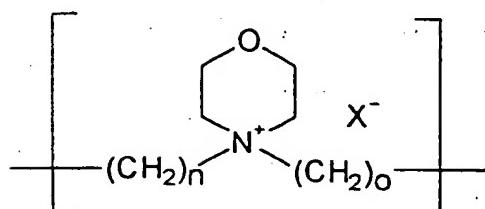
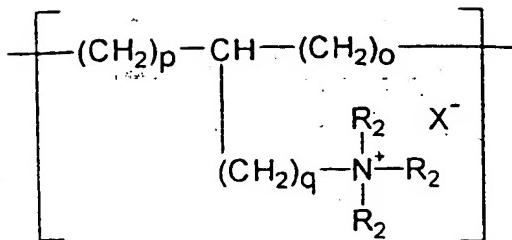
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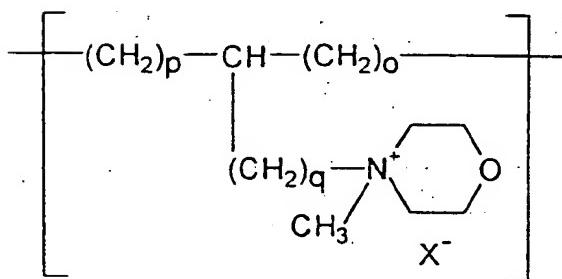
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, or

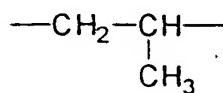


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wherein X represents chlorine or bromine atom, R₂ represents methyl or ethyl, n, o and q independently of one another denote an integer of 1 to 6 and p denotes an integer of 0 to 6;

R_2' and R_3' are identical to or different from each other and represent

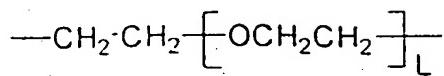
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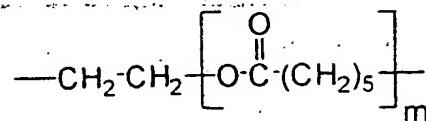


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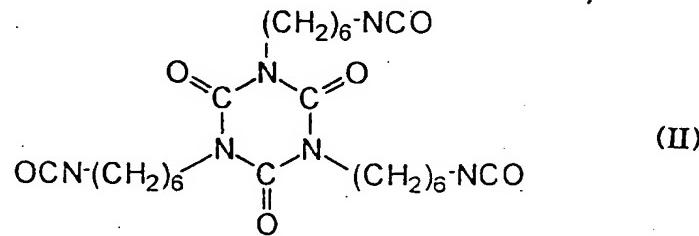
wherein L denotes an integer of 0 to 5, or



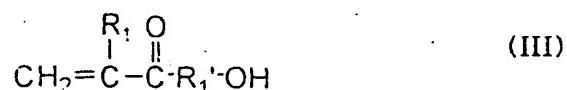
10 wherein m denotes an integer of 1 to 6;
 a, b and c independently of one another represent a real number of 3 or less, provided that they satisfy the conditions of $0 < a \leq 3$, $0 \leq b$ and/or $c < 3$ and $a + b + c = 3$.

15 2. The photo-curable prepolymer according to claim 1 useful as an antistatic agent.

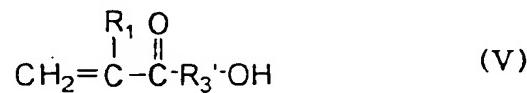
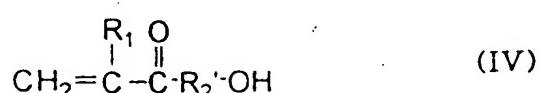
3. A process for preparing the photo-curable prepolymer of formula (I) as defined in claim 1, characterized in that an aliphatic multifunctional isocyanate having the following formula (II) :



is reacted with a quaternary ammonium salt having the following formula (III) :



35 wherein R₁ and R_{1'} are defined as described in claim 1, optionally with a compound of the following formula (IV) and/or that of the following formula (V) :



50 wherein R₁, R_{2'} and R_{3'} are defined as described in claim 1.

4. The process according to claim 3, wherein the hydroxyalkyl (meta)acrylate of formula (IV) or (V) is selected from the group consisting of hydroxyethyl (meta)acrylate, hydroxypropyl (meta)acrylate and hydroxypolyester acrylate.
5. The process according to claim 3, wherein the hydroxy group in the compound of formula (III) is used in a ratio of 1/10 to 2/3 equivalents with respect to the isocyanate groups in the compound of formula (II).



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 4960

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
A,D	EP-A-0 541 289 (WITCO CORPORATION) * the whole document *	1	C08F20/36 C08F120/36 C07D251/34
A	EP-A-0 465 302 (ATOCHEM) * the whole document *	1	
A	EP-A-0 435 211 (UNION CARBIDE CHEMICALS AND PLASTICS COMPANY, INC.) * the whole document *	1	
A	US-A-4 587 201 (TAKAO MORIKAWA ET AL.) * the whole document *	1	
A	US-A-5 322 861 (YUKIO TSUGE ET AL.) * the whole document *	1	
TECHNICAL FIELDS SEARCHED (Int.Cl.)			
C08F C07D			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
BERLIN	23 January 1996	Kyriakakou, G	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	